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COKE REMOVAL OF THE HZSM-12 ZEOLITE WITH DIFFERENT SILICA/ALUMINA RATIO
Kinetic study

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Abstract

The coke removal of HZSM-12 zeolite deactivated in the reaction of *n*-heptane cracking was studied by thermogravimetry using two multiple heating rate integral kinetics models proposed by Ozawa–Flynn–Wall and Vyazovkin to obtain the activation energy of process of thermoxidation of coke. The results obtained by both models presented excellent accordance with the related literature.

Keywords: coke removal, HZSM-12 zeolite, kinetic models, thermogravimetry

Introduction

The reactions of organic molecules on solids catalysts are always accompanied by the formation of secondary products of molecular mass relatively high that are deposited on the surface of the catalyst blocking access to active sites, thereby causing its deactivation. These undesirable organic compounds are usually denominated as 'coke' [1–4].

The deactivation rate depends on several factors [1, 5, 6]: reaction type, temperature, catalyst type, deactivation way (blockade of pores or covering of the active sites). In case of zeolites, the main cause of deactivation is coke deposition in the pores and on the external surface of the catalysts. Rollman and Walsh [7, 8] demonstrated that the coke formation is a reaction with shape selectivity – the coking tendency is an intrinsic property of the zeolite pore structure. However, it is sometimes difficult to distinguish between the effect of pore structure and that originated in acidity on the coking rate of a zeolite. For example, the low coking rate on HZSM-5 that was initially related only to its structure is now ascribed mainly to low density of its acid sites [9]. The ZSM-12 is a high silica zeolite with porous structure formed by a unidimensional 12-membered ring channel system with pore of 5.7×6.7 Å [10]. The

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acidic form of ZSM-12 exhibits activity to several catalytic reactions such as, cracking, hydrocracking and isomerization [11].

A way of fast characterization of coke deposited on a catalyst is through the determination of activation energy (E_a) of coke removal process [12, 13]. The E_a values indicate relative easiness and/or difficulty of coke removal. The coke content of a catalyst can be determined easily by thermal treatment in oxidant atmosphere [14, 15].

In this work, the kinetics of coke removal of several HZSM-12 zeolites with different silica/alumina molar ratio was studied via thermogravimetric measurements. The catalysts were coked through the reaction of *n*-heptane cracking at the temperature of 723 K. The procedure to treat the non-isothermal TG data was carried out by the application of Ozawa–Flynn–Wall [16, 17] and Vyazovkin [18] kinetic models. These models allow the calculation of the activation energy of catalyst regeneration process using dynamic integral TG curves obtained with several heating rates.

Experimental

NaZSM-12 zeolite has been synthesized according to the method proposed by Robson [19], which was adapted for obtained samples with SiO_2/Al_2O_3 molar ratio in gel of 50, 100, 150 and 200, respectively. The materials were synthesized by using the following chemicals as starting materials: silica gel (Merck), sodium hydroxide (Merck), pseudoboehmite (Catapal B – Vista) and methyltriethylammonium chloride (MTEACl – Sigma) as organic template. These reactants were combined to obtain a gel with the following stoichiometric proportion:

$$20MTEA:10Na_2O:xAl_2O_3:100SiO_2:2000H_2O,$$

with x=0.50, 0.67, 1 and 2, respectively. After the preparation of the gel, it was transferred into Teflon lined stainless-steel autoclaves and heated in an oven at the temperature of 140°C under autogenous pressure in static conditions for 6 days.

After synthesis, the materials were calcined for removal of the template, submitted to three successive ion exchange procedures with a 0.6 molar NH_4Cl solution at the temperature of 353 K for 2 h. After this process, they were calcined to 773 K for 3 h to generate the samples in acidic form (denominated of HZSM-12).

The deactivation of the samples of HZSM-12 zeolite by coke deposition was performed in a fixed bed reactor through the reaction of *n*-heptane cracking in the temperature of 723 K and pressure of 101.3 kPa. The *n*-heptane vapors were carried to reactor by flow of nitrogen with a WHSV (mass hourly space velocity) of 20 h^{-1}. The reaction time adopted to deactivation process was 2 h. After the reaction of cracking, the coked catalysts were maintained in flow of pure nitrogen for 1 h in the same reaction temperature to the removal of all volatiles molecules of porous of the zeolite.

To study the kinetics of coke removal the samples of coked HZSM-12 were submitted to thermogravimetric analysis in a thermobalance Mettler-STGA 851, from room temperature to 1173 K, under synthetic air flow (25 mL min^{-1}) and heating rates (β) of 5, 10 and 20 K min^{-1}. For each experiment ca. 10 mg of deactivated catalyst was used. The Ozawa–Flynn–Wall and Vyazovkin kinetics model was applied to study the coke removal process.

Results and discussion

The acidity properties of the samples of HZSM-12 were evaluated through the *n*-butylamine thermodesorption, where the quantity of base desorbed per grams of zeolite indicates the number of acid sites (acid sites density) and the temperature range of desorption can be related to acid strength (medium or strong acid sites), as indicated in Table 1. The acidity measurements revealed that the total number of acid sites (medium and strong) decrease with the increase of the SiO_2/Al_2O_3 molar ratio at samples.

Table 1 Acidic properties of the samples of HZSM-12 zeolite obtained through thermodesorption of *n*-butylamine

Sample[a]	Medium acid sites		Strong acid sites	
	ΔT/K	Acidity/mmol g^{-1}	ΔT/K	Acidity/mmol g^{-1}
HZ-50	387–607	0.27	607–880	0.34
HZ-100	385–613	0.25	613–877	0.14
HZ-150	388–593	0.11	593–879	0.17
HZ-200	391–609	0.12	609–877	0.19

[a] HZ-*n*, where ‘*n*’ represents the SiO_2/Al_2O_3 molar ratio in the gel of synthesis

The TG/DTG curves of coke burning process obtained in heating rate of 5 K min^{-1} in dry air flow (25 mL min^{-1}) are shown in Fig. 1. It may be noted that the temperature range for coke removal as identified by DTG curves was practically identical to all the samples. The percentages of coke deposited on the materials were

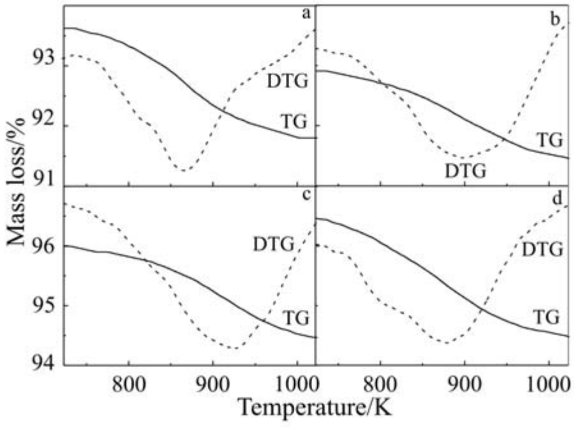

Fig. 1 TG/DTG curves of coked HZSM-12, obtained in air flow (25 mL min^{-1}) and heating rate of 5 K min^{-1}. a – HZ50, b – HZ100, c – HZ150 and d – HZ200

determined through TG curves; assuming that the mass loss in the temperature range 723–1023 K it is exclusively related to coke removal (Table 2). The quantities of coke formed on the HZSM-12 samples decrease with the increase of the SiO_2/Al_2O_3 molar ratio of materials. This can be explained by considering that the increase in SiO_2/Al_2O_3 molar ratio causes the decrease of the number of acid sites, which are mainly responsible for the coke deposition.

Table 2 Temperature range to coke removal and mass percentage of coke removed of the samples of coked HZSM-12

Sample	Temperature range/K	Coke/%
HZ-50	723–1023	1.82
HZ-100	723–1023	1.45
HZ-150	723–1023	1.53
HZ-200	723–1023	1.31

To calculate the activation energy of coke removal through Ozawa–Flynn–Wall [16, 17] method Eq. (1) was used:

$$E_a \cong -18.2\frac{\partial \lg\beta}{\partial(1/T)} \quad (1)$$

where β is the heating rate (K min^{-1}), T is the absolute temperature (K) and E_a is activation energy (kJ mol^{-1}). Therefore a plot lgβ *vs.* $1/T$ to several conversion degree of the process must be a straight line (Fig. 2) with the angular coefficient equal to the $\partial\lg\beta/\partial(1/T)$ permitted calculate E_a via Eq. (1).

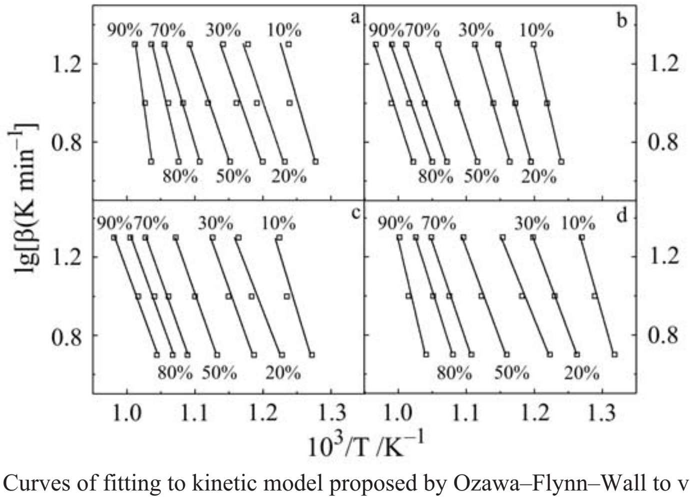

Fig. 2 Curves of fitting to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages. a – HZ50, b – HZ100, c – HZ150 and d – HZ200

To obtain the activation energy of coke removal through a kinetic model proposed by Vyazovkin [16] Eq. (2) was used:

$$\ln\left(\frac{\beta}{T^2}\right)=\ln\left[\frac{AR}{F(\alpha)E_\mathrm{a}}\right]-\frac{E_\mathrm{a}}{RT} \tag{2}$$

where β is the heating rate (K min^{-1}), T is the absolute temperature (K), A is the pre-exponential factor, $F(\alpha)$ is function unknown of the conversion; R is the gas constant and E_a is activation energy (kJ mol^{-1}). Therefore a plot $\ln(\beta/T^2)$ *vs.* $1/T$ to several conversion degree α, must be a straight line (as shown in Fig. 3) with the angular coefficient equal to the $-E_\mathrm{a}/R$.

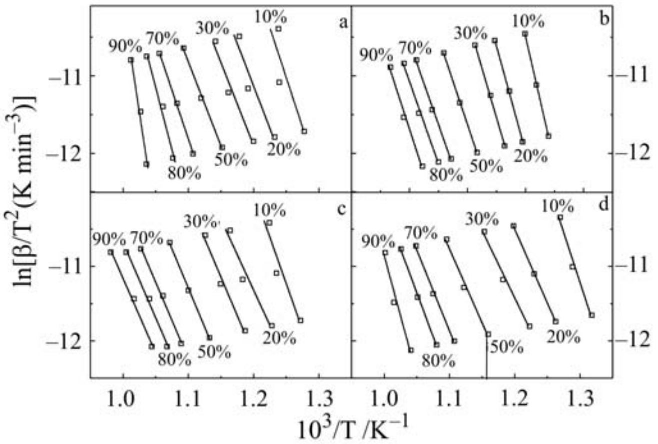

Fig. 3 Curves of fitting to kinetic model proposed by Vyazovkin to various conversion percentages. a – HZ50, b – HZ100, c – HZ150 and d – HZ200

As indicated in Table 3, the values of E_a calculated by the two methods presented an excellent accordance, evidencing that both models can be used to describe kinetics of coke removal by thermogravimetry.

Table 3 Values of activation energy obtained by Ozawa–Flynn–Wall and Vyazovkin models

Sample	Activation energy*/kJ mol^{-1}	
	Ozawa–Flynn–Wall model	Vyazovkin model
HZ-50	183	187
HZ-100	188	187
HZ-150	178	168
HZ-200	185	171

*The activation energy were calculated as arithmetic average of the several E_a values obtained in different conversion degree shown in the Figs 2 and 3

The values of the activation energy reported in [20], for the combustion of coke formed in different processes and on several types of catalysts are between 125 and 175 kJ mol^{-1}, with the high values of E_a (ca. 175 kJ mol^{-1}) be attributed to coke formed in reactions poor in hydrogen, as the cracking of hydrocarbons [12]. This way, the values of the activation energy obtained by the two models used in this study (in the range of 173–188 kJ mol^{-1}, as indicated in Table 3), are in excellent accordance with the related literature.

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